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## Initial stages of growth and formation of $\text{CaF}_2$ nanostructures on Si(001)

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### Introduction

Stimulated by a number of potential applications [1], growth of fluorite ( $\text{CaF}_2$ ) on Si(111) has been extensively studied [2]. Only a few attempts have been undertaken, however, to investigate the initial stages of  $\text{CaF}_2$  growth on a technologically important Si(001) surface [3, 4], where anisotropic  $\text{CaF}_2$  growth accompanied by the formation of the quasi-one-dimensional islands was observed using TEM and STM techniques. Such islands with nanometer scale width could be attractive for nanolithography. In this work we studied the initial stages of the fluorite growth and the formation of nanometer-scale islands on Si(001) using electron diffraction (RHEED and LEED), atomic force microscopy (AFM), ultra-violet photoemission spectroscopy (UPS) and metastable atom deexcitation spectroscopy (MDS).

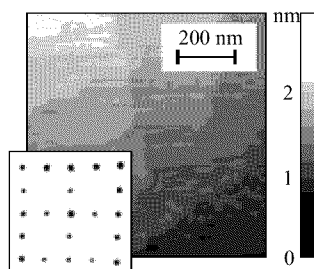
### 1. Experimental

Calcium fluoride nanostructures have been grown in the UHV conditions by evaporation of  $\text{CaF}_2$  small pieces in an amorphous carbon crucible onto a thermally cleaned at  $1250^\circ\text{C}$  Si(001) surface. The temperature of the substrate during the fluorite deposition was in  $400\text{--}750^\circ\text{C}$  range, the deposition rate was  $2\text{--}3\text{ nm/min}$ . Electron energies in RHEED and LEED measurements were  $15\text{ keV}$  and  $70\text{ eV}$  respectively. The surface morphology of the  $\text{CaF}_2/\text{Si}(001)$  structures was measured *ex-situ* in the tapping mode of a P4-SPM atomic force microscope produced by NT-MDT (Zelenograd, Russia). The typical lateral resolution of the AFM measurements was  $10\text{--}20\text{ nm}$ , depending on the sharpness of the cantilever tip. In the UPS experiments a He windowless differentially pumped discharge lamp emitting He I ( $21.2\text{ eV}$ ) photons and a hemispherical electron analyzer have been used. In the MDS a differentially pumped discharge nozzle-skimmer source was used.

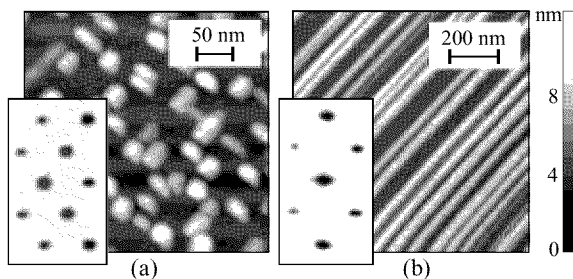
### 2. Results and discussion

Before the fluorite deposition, electron diffraction patterns clearly showed  $2 \times 1$  and  $1 \times 2$  domains (see for example inset in Fig. 1). Atomic force microscopy showed  $100\text{--}200\text{ nm}$  width terraces separated by steps of 1 to 8 monolayers (ML) height (Fig. 1). Depositing a few  $\text{CaF}_2$  monolayers (typically  $1\text{--}6\text{ ML}$ ) at this surface, we found that the surface morphology drastically changed with the temperature of the Si(001) substrate.

After the growth at  $450^\circ\text{C}$ , an array of more or less uniformly distributed  $\text{CaF}_2$  islands with characteristic size of  $10\text{--}20\text{ nm}$  (Fig. 2(a)) could be seen on the surface. The islands were  $3\text{--}8\text{ nm}$  in height and most of them were elongated in the  $[110]$  or  $[1\bar{1}0]$  directions. The transmission spots on the RHEED patterns taken along these directions (inset in Fig. 2(a)) showed that the lattice orientation in the silicon substrate coincided with that of the fluorite islands. It is noteworthy that during the  $\text{CaF}_2$  growth the Si(001)  $2 \times 1$  superstructure



**Fig. 1.** AFM topography image of Si(001) substrate before  $\text{CaF}_2$  deposition. Inset — LEED pattern of the surface taken at 70 eV.



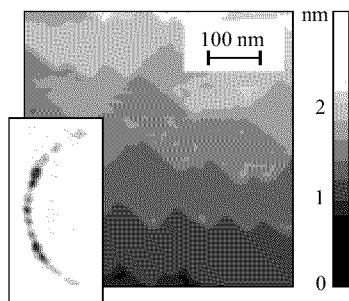
**Fig. 2.** AFM topography images after deposition of one  $\text{CaF}_2$  monolayer at  $450^\circ\text{C}$  (a) and 6 ML at  $650^\circ\text{C}$ . Insets — corresponding RHEED patterns.

disappeared gradually: it could be distinguished in the pattern even after 2–3 ML of  $\text{CaF}_2$  were deposited.

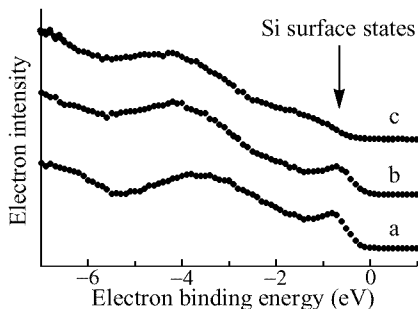
Increasing the deposition temperature above  $700^\circ\text{C}$ , a different type of nanostructures was obtained. The fluorite forms an array of very narrow parallel stripes of several microns length (Fig. 2(b)), running along either the  $[110]$  or  $[1\bar{1}0]$  directions, depending on which direction was closer to the surface steps on Si. At intermediate temperature, however, structures with two perpendicular arrays could be observed. The width of the stripes was 15–20 nm, measured by AFM, and their height was 3–8 nm. Since the earlier stages of deposition, the RHEED pattern taken with the e-beam perpendicular to the stripes (inset in Fig. 2(b)) showed distinct transmission spots which were different from the low-temperature case (see inset in Fig. 2(a)). The pattern indicated that  $\text{CaF}_2$   $[110]$  axis was normal to the substrate plane while the  $\text{CaF}_2$   $[1\bar{1}0]$  axis coincided with Si  $[1\bar{1}0]$ . The RHEED pattern taken with the e-beam parallel to the stripes showed the  $3 \times 1$  reconstruction, reported earlier [5] for  $\text{CaF}_2$  growth on the Si(110) surface. This fact was another evidence for the unusual (110) orientation of the  $\text{CaF}_2$  lattice.

A detailed analysis of the RHEED pattern evolution during the high-temperature growth has shown that the stripes form after the deposition of a single  $\text{CaF}_2$  monolayer. Unlike thicker structures, the first  $\text{CaF}_2$  monolayer covered the substrate uniformly, acting as a wetting layer (Fig. 3). During the formation of the wetting layer the surface remained flat. However, a drastic change of the surface step pattern took place. Instead of the ill-defined shape of the step edges on the initial silicon surface, the step edges of the wetting layer were aligned along the  $[110]$  or  $[1\bar{1}0]$  directions. During the wetting layer formation, in the direction where the stripes were expected to develop at higher  $\text{CaF}_2$  coverage, one could observe a  $3 \times 1$  superstructure in the RHEED pattern (inset in Fig. 3).

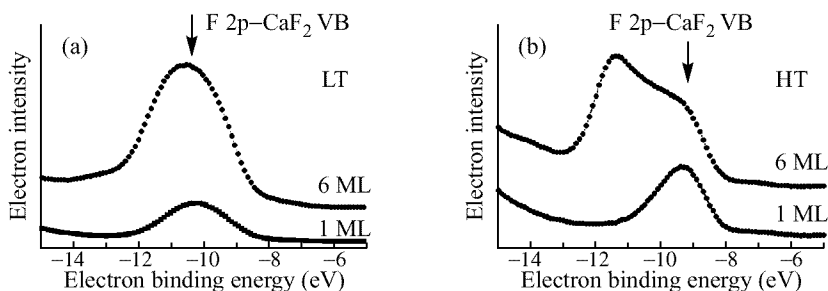
MDS and Photoemission measurements with He I photons allowed us to monitor the formation of new bonds at the interface. Figure 4 (curves a and b) shows that the intensity of the Si surface state peak after the deposition at low temperature ( $450^\circ\text{C}$ ) practically has not change, indicating that the most part of the surface keeps the silicon superstructure. This correlates with the observation of the Si(001)  $2 \times 1$  superstructure in the RHEED patterns even after the deposition of 2–3 ML of  $\text{CaF}_2$ . These findings allowed us to conclude that the area between the  $\text{CaF}_2$  dots (see Fig. 2(a)) was bare silicon surface. However, after the deposition of one  $\text{CaF}_2$  monolayer at high temperature ( $700^\circ\text{C}$ ) the silicon surface state peak disappeared (Fig. 4(c)). This correlates with the formation of the wetting layer uniformly covering the silicon surface. It is believed that the wetting layer results from the



**Fig. 3.** AFM topography image of the wetting layer formed after fluorite deposition at 750°C. Inset — RHEED pattern.



**Fig. 4.** Ultraviolet photoemission spectra in Si valence band region: (a) bare Si(001)  $2 \times 1$  surface; the same surface covered with 1 ML of  $\text{CaF}_2$ : (b) at 450°C; (c) at 700°C.



**Fig. 5.** Ultraviolet photoemission spectra in  $\text{CaF}_2$  valence band region after  $\text{CaF}_2$  deposition at 450°C (a) and 700°C (b).

chemical reaction at the interface with the creation of strong chemical bonds and change in calcium ion charge, somewhat similar to what is observed in  $\text{CaF}_2/\text{Si}(111)$  [7].

Also from MDS measurements it was evident that a part of the substrate remained unreacted when deposition occurred at low temperature, since contributions from Auger neutralization [5] from clean Si were observed on the experimental spectrum. On the other hand, after the completion of 1 ML at high temperature, MDS showed the formation of a distinct low binding energy band that could be associated to the Ca  $4s$  states. In this case no contributions from the substrate were observed.

UPS spectra at increasing  $\text{CaF}_2$  coverage (Fig. 5) were drastically different for low-temperature and high-temperature growths. At low temperature deposition (Fig. 5(a)) the position of F  $2p$  line was almost independent on the  $\text{CaF}_2$  coverage: this could be explained in terms of the 3D growth mode observed in RHEED from the initial stages of deposition. The slight shift to the higher binding electron energy and the broadening of the peak could be associated to an increase of the average size of the  $\text{CaF}_2$  dots.

As was mentioned above, at high temperatures and submonolayer coverage, the formation of reacted fluoride wetting layer took place. The considerable shift ( $\sim 1$  eV) to the lower binding energies of the fluorine peak (Fig. 5(b), lower curve) could be associated to the difference from the bulk fluorine environment in this layer. Drastic transformations of the photoemission spectra at larger coverage and high deposition temperature (Fig. 5(b), upper curve) could be naturally related with the formation of a bulk-like valence band in the fluoride stripes observed in RHEED and AFM (see Fig. 2(b)). A similar effect was

observed in the  $\text{CaF}_2/\text{Si}(111)$  system after the deposition of a  $\text{CaF}_2$  layer as thin as 2.5 ML.

One of the puzzling phenomena observed in our experiments was the formation of the single array of the parallel fluorite stripes on the initially two-domain  $2 \times 1$  and  $1 \times 2$  surface. The well-pronounced two-fold anisotropy of the RHEED patterns taken from the wetting layer provided a strong evidence for the transformation of the surface symmetry from four- to two-fold during the formation of the wetting layer. We found that several  $\text{CaF}_2$  MLs deposited on the wetting layer at low temperature resulted in the formation of the stripes rather than dots. The RHEED pattern taken in the azimuth across these stripes obtained at low temperature showed that the  $\text{CaF}_2$  lattice was oriented in the same way as in the high-temperature stripes, i.e. with the  $\text{CaF}_2$  axis normal to the substrate. This was an additional evidence of the key role played by the wetting layer in the formation of the fluoride stripes.

Another attractive issue was clarifying the driving forces for the formation of so narrow and long fluorite stripes. Taking into account that in the fluorite structure (111)-surface has the minimum energy [1], one could expect that both  $\text{CaF}_2$  islands and stripes were formed by (111) facets. Though the resolution of the AFM was not sufficient to confirm this, in the RHEED patterns, at certain diffraction conditions, inclined streaks expected for such facets were clearly seen. From the RHEED data one could conclude that a good lattice matching existed only along the stripes, but across the stripes a mismatch as high as 45% was expected. This is one of the possible reasons for the observed growth anisotropy. Another probable reason of the long fluorite stripes formation could be due to the diffusion anisotropy of the  $\text{CaF}_2$  molecules on the surface of the wetting layer. One more reason of the anisotropy in  $\text{CaF}_2$  growth could be related to the fact that the ends of the stripes are formed by the vertical (111) facets. The molecules, which attach the stripes in the base of these facets, form a larger number of bonds than the molecules at the base of the inclined facets. This would also favor the preferential growth along the stripes.

#### Acknowledgements

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